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For an explanation of the two-letter codes, and other abbreviations, the reader is referred to the explanations ("Guidance Notes on Codes and Abbreviations") at the beginning of every regular publication of the PGT Gazette.

Title: DISCONTINUOUS POLYTRIMETHYLENE TEREPHTHALATE FIBERS AND METHOD FOR PRODUCING THE SAME

Abstract: The present invention relates to discontinuous polytrimethylene terephthalate fibers characterized by a new combination of properties. The association of new stress-elongation and modulus properties enables the production of discontinuous fibers, textiles or household fabrics having very high aesthetic qualities and utility values. The invention also relates to an economical method in two steps for producing said discontinuous polyethylene terephthalate fibers. Fusion spinning is carried out at a high polymer flow rate and at a running speed of at least 600 m/min. The drawing, thermal setting, creping and drying steps are carried out on a separate drawing bench.

DISCONTINUOUS POLYTRIMETHYLENE TEREPHTHALATE FIBERS AND METHOD FOR PRODUCING THEM

Description:

The present invention concerns discontinuous PTT fibers [where PTT is equal to poly(trimethylene terephthalate)] and a process for producing them in a two-step spinning and stretching process.

Discontinuous fibers made of polyethylene terephthalate and melt spinning units for producing them are known (Fourné, Synthetic Fibers, Hanser Verlag [1995] pages 460 - 462). Due to its different crystallization behavior, these processes are not easily transferable to PTT.

Processes for the production of continuous PTT filaments have also been described. Thus the Journal of Polymer Science, part A-1, vol. 4, 1851-1857 (1966) mentions PTT fibers among others. The high stretching ratios that are mentioned imply an uneconomically low spinning speed. The listed fiber characteristics do not correspond to today's market requirements.

EP 0 547 553 A1 describes the production of monofilaments at a spinning speed of 20 m/min and a production speed of 100 m/min.

EP 0 754 790 A2 describes the production of textile filaments of PTT among others by means of heating surfaces heated to high temperatures as stretching aids. Concrete design examples are provided.

WO 99/11845 A1 describes PTT fibers, wherewith a birefringence of at least 0.030 is obtained. The listed property data indicate low elongations to rupture of 90%, which do not allow for a sufficiently high stretching ratio for subsequent processing to produce discontinuous fibers and are thus unsuitable.

WO 99-21168 A1 discloses a high-speed spin stretching process for the production of PTT filaments, which are wound on spools. High throughputs and cable deposition rates for the production of discontinuous fibers cannot be derived therefrom.

CA 86:122866 of JP 52-08124 A relates to the treatment of PTT multifilaments with heating devices, where an elongation of 33%, which is to be applied, is unsuitable for discontinuous fiber production.

CA 86:122865 of JP 52-08123 A describes the application of an desirable high elongation ratio of 300% in the production of PTT fibers. However, the spinning speed of 360 m/min that is practiced in addition is so low that the economy of the process is questionable.

CA 86:122856 of JP52-05320 A describes the spinning of PTT, where the elongation ratio that is practiced indicates uneconomically low spinning speeds.

It is the object of the present invention to make available discontinuous PTT fibers, such that these and the textiles and household textiles produced from them, in particular carpets, should have a high degree of aesthetic and value in use properties as well as environmentally friendly dying properties compared with conventional fibers. The production of these discontinuous PTT

fibers should take place in a two-step process of melt spinning and stretching, which is more economical than the aforementioned processes for continuous filaments.

According to this invention, this task is accomplished by means of discontinuous PTT fibers as well as a process for the production of discontinuous PTT fibers with an intrinsic viscosity of at least 0.70 dl/g as specified in the claims.

PTT here signifies a polyester with at least 90 mole-% of trimethylene terephthalate units. Suitable comonomers are isophthalic acid, 2,6-naphthaline dicarboxylic acid, ethylene glycol, diethlyene glycol, 1,4-butane diol, 1,4-cyclohexane dimethanol. Poly(trimethylene terephthalate) homopolymer is preferred and particularly preferred is the polymer containing a low fraction of ether groups formed during the production process and derived from the 1,3-propane diol. The intrinsic viscosity of the discontinuous PTT fibers is in the range of 0.7 to 1.3 dl/g and particularly preferably about 0.75 to 1.15 dl/g.

One starts with a PTT melt, which is either removed directly from the polycondensation reactor for PTT production or which is obtained by melting a PTT granulate. The polymer melt can contain the usual additives, such as dyes, delustering agents, stabilizers, antistatics, lubricants, branching agents, in total amounts of 0 to 5.0 wt-%, or the additives can be added to the melt on its way to the spinnerets. Additives, which noticeably affect structural properties (e.g., the elongation to rupture of the spun fiber), are excluded.

According to this invention, the production of discontinuous PTT fibers, preferably with a titer of 0.8 to 20, occurs in a two-stage spinning and stretching process, which comprises the following steps:

1. The PTT melt having a polymer melting point T_m is supplied to the spinning system at a melt temperature $T_s = T_m + k$ (°C), where 7 k 63, preferably 23 k 41. The transport and distribution of the melt to the spin bar occurs through double walled product lines, which are heated to a temperature of 234 to 290 °C with a liquid and/or vaporous heat exchanger medium in the outer shell of the lines. Other heating methods are possible. The wall shear rates of the melt in the line system are 2 to 128 sec^{-1}, preferably 3.5 to 16 sec^{-1} in the pipe lines and 12 to 128 sec^{-1} in static mixing elements, which are installed within certain line sections. The shear rate γ is herewith defined by the shear rate in the empty pipe times the mixer factor m, where the mixer factor is an inherent characteristic of the mixer type and is equal to about 3.5 – 4 for Sulzer SMXL mixers. The shear rate γ in sec^{-1} is calculated in accordance with

$$\gamma = \frac{4 \cdot 10^3 \cdot G}{\pi \cdot \delta \cdot R^3 \cdot 60} \cdot m$$

where G = polymer feed rate (g/min),
S = nominal polymer density (g/cm^3),
R = empty tubing radius [mm].

The average retention time of the melt in the product line up to entry into the spin bar is maximally 30 min, preferably maximally 25 min. The line temperature T_L is preferably set within the above limits such that it is in the range $T_L = T_s \pm 15$ °C. The product line optionally contains at least one booster pump, at least one polymer filter, at least one polymer heat exchanger and at least one shut off and a distributor fitting.

2. The PTT melt in the spinning bar is supplied to at least one spinning pump, then, by means of the pressure produced by the pump and at a constant feed rate set by selection of the pump speed, supplied to at least one spinneret packet, within the spinneret packet, pressed through distributor devices, filtering and shearing media and finally spun to form melt threads through holes in the spinneret plate. The nozzle holes can be round or of any other geometry.

   The spinneret package can be inserted into the spin bar from the bottom and can have a cylindrical geometry, while the nozzle holes are symmetrically distributed over a circular area in the injector plate.

   The injector plates have a hole density of 0.3 to 20 holes/cm^2. The nozzle hole diameter D is selected as a function of the nozzle hole throughput according to

$$\sqrt{\frac{F(g/min)}{\zeta(g/cm^3)\cdot\pi\cdot 2}} \geq D(mm) \geq \sqrt{\frac{F(g/min)}{\zeta(g/cm^3)\cdot\pi\cdot 7}},$$

   where ζ is the density of the melt and is equal to 1.11 g/cm^3 for homo-PTT.

   The feed rate F per nozzle hole, related to the fiber titer, lies in the range of F(g/min)/titer(dtex) = (0.14 to 0.66).

   The retention time of the melt in the nozzle packet is maximally 4 min. The spin draft is selected between 1 : 30 and 1 : 160 and is determined in a known manner from the ratio of the draw-off speed to the extrusion speed at the nozzle holes.

   The heating of the spin bar is selected the range of 234 - 290 °C such that the following relationship applies: T_B (°C) = T_s + dT_w + 4/100 dp(bar) ± 15, where dT_w = change of the melt temperature in the heat exchanger, which is made to be positive for heating and negative for cooling and is equal 0 in units without heat exchangers, dp(bar) = total to pressure drop of the melt up to its exit from the spinneret plate.

3. The cooling of the melt threads occurs by means of turbulence-free cooling air flowing in vertically with respect to the direction of travel of the thread at a temperature between 5 and 25 °C, preferably 8 to 18 °C. The average flow rate of the cooling air from the rectifier is 0.5 to 2.0 m/sec. The lengths of the air cooling zones are between 50 and 2000 mm, preferably 150 to 600 mm in the case of air cooling systems (radial cooling) that are concentric to the thread direction, and 500 to 2000 mm in the case of air tunnels with a transverse air stream, and particularly preferably 150 - 300 mm for fiber titers 5 den/filament and 300 to 600 mm for 12 - 20 den/filament.

4. The preparation of the cooled spun threads occurs with an oil-water mixture. The quantity of water on the threads is set to between 12 and 30 wt-%, preferably 18 to 25 %.

   Immediately or shortly thereafter, the filaments of a spin position are combined to a filament bundle. Subsequently, the filament bundles of the individual positions are combined to a spin cable, preferably at the spinning wall. The draw-off of the spin cable occurs at speeds in the range of 600 to 2000 m/min by means of a draw-off device, followed by deposition of the spin cable in a can.

5. The cans are assembled into a creel in a creel space held at a controlled temperature of 15 °C to 35 °C, preferably 20 °C to 27 °C and are supplied to a drawing bench. The draw-off of the spin cables from the cans is accomplished with an intake device, whereupon at least one full cable is formed from individual spin cables by means of a comb.

   The whole cables are stretched in at least one stretching step, possibly while supplying a controlled temperature oil-water mixture. The temperature for this process is maintained at 20 - 100 °C. The stretching ratio (SR) is selected according to spun thread elongation R_d such that $SR(\%) = 1 + \alpha \quad Rd/100$, where $\alpha = 0.25$ to 0.75, where smaller α-values are preferred for big titers and larger α-values for smaller titers.

   Subsequently, depending upon the applied temperature of maximally 210 °C, optional thermofixing and relaxation occur in at least one step. The stretching, thermofixing and relaxation occur at speeds of 25 to 400 m/min.

   The exit speed from the relaxation zone is preferably at least 90 m/min, particularly preferably 180 m/min with titers 5 dtex.

   The cooling of the whole cable to below the glass transition temperature is preferably accomplished with an oil-water mixture and/or with pure water.

6. Subsequently, the partial cables are assembled into at least one cable and these are supplied to one stuffing chamber creping machine per cable. An optional post-brightening with an oil-water mixture and/or steaming of the cable occurs as an aid to creping. The subsequent drying of the cable in at least one dryer stage occurs with retention times of 0.5 to 10 min, at temperatures of 30 to 200 °C, preferably 60 to 165 °C. Cutting of the resulting cable(s) to a pile length preferably between 6 and 200 mm can follow. Alternatively, there is the possibility of packing the cable(s) and of processing it (them) to discontinuous fibers in a later storage operation.

   In this way, discontinuous PTT fibers are obtained having a new combination of properties previously not known for discontinuous fibers, which are as follows: a high permanent elasticity and bulkiness of the fibers, a new combination of high viscosity in combination with the mechanical parameters described by the stress-elongation curve, of modulus values and thermal shrinkage stability, where dying with dispersion dyes is possible without the addition of carrier/dye absorption aids, and the fibers have permanent spot-rejecting characteristics.

   A LASE value of 5 to 12 cN/tex at an elongation of 10 %, a secant modulus at an elongation value = elongation to rupture minus 45% (but at least 5 %) of less than 1.0 cN/tex per 1% change in elongation and a creping resistance of over 75 % is characteristic of the discontinuous PTT fibers of this invention. This combination of properties leads to an aesthetic and a utility value which is extremely desirable in comparison with conventional fibers. The dying properties provide a substantially better environmental compatibility of the post-processing procedure. The areas of application are in fabrics and household fabrics, in particular in carpets.

   The invention is described in greater detail in the following examples, without limiting the invention to these example embodiments.

Example 1:

PTT cuttings with an I.V. of 0.93 dl/g, a melting point T_M = 227 °C and a water content of 20 ppm were melted to a melt at 255 °C in an extruder, and this melt was pressed into a spinning system through a product line at the same temperature. Three SMXL type mixers of the Sulzer/Schweiz Company were installed in the product line, wherewith the shear rate in the mixers was 28 sec^{-1} with a polymer throughput of 2500 g/min. The pipe diameter was selected such that the shear rate in the open line was 7.9 sec^{-1}. The average retention time in the product line was approximately 3 min.

The spinning of the PTT melt took place in a spinning system BN 100 of the Lurgi Zimmer AG Company with an annular injector plate and a radial cooling tunnel. The hole density of the spinneret plate was 6.3 holes/cm^2. The spin bar temperature was 256 °C, wherewith the total pressure drop of the melt up to the exit from the spinneret was 140 bar. Heat exchangers were not installed. The retention time in the nozzle package was approximately 0.5 min.

The melt threads exiting from the injector plate were cooled by means of cooling air introduced radially from the outside toward the center at a rate of 1400 Nm^3/h and at a temperature of 8 °C. The solidified spun threads were applied to a ring lubricator at a distance 850 mm from the bottom of the injector plate and acted upon by a water-oil mixture, so that the quantity of water on the spun threads was about 25 wt-% and a very stable thread flow was obtained. The spin draw-off speed was 900 m/min. After being drawn off, the spun threads were deposited into cans in the form of spin cables by means of a winder.

The separate stretching of the spin cables in a drawing bench took place in two steps. Subsequently, the spin cables were thermofixed with slight relaxation, cooled, creped, dried and cut to discontinuous fibers. The production speed in the drawing bench, corresponding to the speed of the roller system at the exit from the final stretching zone, was 100 m/min.

Further processing parameters and the textile properties of the discontinuous fibers are listed the table. It should be noted that, due uncertainties of the measurement, relaxation in the can or water/oil application, the measured titer can deviate from the theoretical value by up to ± 5 %. The discontinuous fibers could be dyed at 95 °C with dispersion dyes, such as Terasil Navy Blue GRL/C from Ciba/CH, without the addition of carrier/dye absorption aids.

The intrinsic viscosities (IV) were measured with a solution of 0.5 g PTT in 100 ml of a mixture of phenol and 1,2-dichlorobenzene (3 : 2 parts by weight) at 25 °C.

The melting points and glass transition temperature were determined by means of DSC with a heating rate of 10 °C/min, after the sample had been melted briefly before and quenched immediately thereafter.

The titer and stress-elongation properties of the fibers were determined with the instrument set, Vibrotex and Vibrodyn of the Lenzing Company/Austria. The clamping length was 20 mm, the pre-tensioning weight was dependent on the titer, 100 mg/dtex and the test speed was 20 mm/min.

The LASE (load at specific elongation) values could be determined directly at the test device by inputting the reference elongations. The secant module was determined by applying a secant to the elongation value = (elongation to rupture minus 45 %, but at least 5 %), and the slope of these straight lines in (cN/tex) with respect to a 1 % change in elongation was evaluated.

That hot-air-shrinkage was determined in an oven at a temperature of 180 °C with a retention time of 20 min without pre-stressing the fiber. .

The crimping arcs were counted visually. The crimping values were determined according to the method of and with the Vibrotex device from Lenzing/AT.

Example 2:

Discontinuous fibers of carpet quality with a titer of 17 dtex were produced according to the methods of the example 1, but taking into consideration of the parameters listed in the table, and the results are listed in the table.

The fibers characterized by having outstanding bulking and crimping recovery behavior.

Table

Example No.		1	2
PTT Melting point T_m	°C	227	227
PTT Glass transition	°C	46	46
PTT - I.V.	dl/g	0.93	0.93
Melt temperature T_s	°C	255	255
Line temperature T_L	°C	255	255
Shear rate line	sec^{-1}	7.9	7.9
Shear rate mixer	sec^{-1}	28	28
Temperature change in the heat exchanger	dT_w °C	0	0
Total pressure loss	dp(bar)	140	175
Spin bar temperature	°C	256	256
Hole density injector plate	n/cm^2	6.3	1
Delivery rate per nozzle hole	g/min	0.668	4.15
Spin draft	1:	77	12
Air cooling tunnel length	mm	200	300
Cooling air temperature	°C	8	8
Cooling air amount	Nm^3/h	1400	1500
Average cooling air velocity	m/sec	1.5	1.1
Spin preparation concentration	%	0.5	0.5
Draw-off speed	m/min	900	800
Drawing bench intake speed	m/min	32.8	19.2
1st Stretching zone temperature	°C	57	57
Stretching zone stretching ratio	1:	2.7	3.4
2nd Stretching zone temperature	°C	70	80
Stretching zone stretching ratio	1:	1.13	1.15
Fixation zone temperature	°C	90	100
Fixation zone relaxation ratio	1:	0.94	1.00
Exit speed relaxation zone	m/min	94	75
Dryer temperature	°C	70	150
Dryer residence time	min	2.5	2.5
Total stretching ratio	1:	3.05	3.91
Actual relaxation ratio of the fiber	1:	0.90	0.74
Spun threads	dtex	7.87	50.6
- titer			
- tear strength	cN/tex	13.9	10.7
- elongation to rupture	%	314	613
- I.V	dl/g	0.90	0.90
- density	g/cm^3	1.3207	1.3178
Discontinuous fibers			
- titer	dtex	3.05	17.2
- CV titer	%	5	5.3
- tear strength	cN/dtex	35.8	28.0
- elongation to rupture	%	54.9	72.4
- CV elongation to rupture	%	9.2	12.1
- LASE (2 %)	cN/tex	3	2.5
- LASE (5 %)	cN/tex	6	5
- LASE (10 %)	cN/tex	7.9	7.2
- secant modulus (R_d –45%)	cN/tex per 1 %	0.5	0.32
- number of crimping arcs	n/cm	11	13
- creping value	%	12	13
- creping stability	%	86	81
- hot air shrinkage	%	16	3
- cutting length	mm	38	150

According to the process that is described, it is also possible to produce different titers, in particular finer titers such as microfilaments down to 0.8 den and less. The titer can thus be decreased according to methods known to the specialist, by lowering the melt throughput through the spinneret or increasing the number of nozzle holes wile holding the throughput constant.

Claims:

1. Discontinuous PTT fibers, characterized by the fact that they have an intrinsic viscosity in the range of 0.70 - 1.3 dl/g, a LASE (10 %) of 5 to 12 cN/tex, a secant modulus (R_d - 45 %) of < 1.0 cN/tex per 1 %, a creping stability > 75 % and are dyable with dispersion dyes without the addition of carrier/dye absorption aids.

2. Discontinuous PTT fibers in accordance with claim 1, characterized by the fact that they have an intrinsic viscosity in the range of 0.75 to 1.15 dl/g and a titer in the range of 0.8 to 20 den.

3. Process for the production of discontinuous PTT fibers with an intrinsic viscosity of at least 0.70 dl/g by means of a two-stage spinning and stretching process, characterized by the fact that

   a) a PTT melt with a temperature T_s (°C) = T_M + k, where T_M is the melting temperature of the PTT and 7 k 63, is supplied, via a product line that is heated to a temperature T_L in the range of 234 to 290 °C by means of an external heat distribution medium, to a spinning bar heated to a temperature T_s of 234 to 290 °C, with at least one spinning pump, a spinneret package and an injector plate with a hole density of 0.3 to 20 holes/cm^2, each in the flow direction, and is spun through the single injector plate to produce melt threads, where the average retention time of the PTT melt in the product line is less than 30 min and in the spinneret package is maximally 4 min and the spinning draft is 1 : 30 to 1 : 160, and the feed rate F in g/min per nozzle hole per unit of the fiber titer in dtex lies in the range 0.14 to 0.66,

   b) the melt threads are cooled with turbulence-free cooling air at 5 to 25 °C, flowing vertically to the direction of travel of the thread at an average air outlet speed of 0.5 to 2.0 m/sec in a cooling zone having a length of 50 to 2000 mm, and the cooled threads are acted upon with a water oil mixture such that 12 to 30 wt-% of water remains on the threads, and the threads are combined into filament bundles, which are in turn combined into spin cables, which are drawn off with a draw-off speed in the range of 600 to 2000 m/min and put into cans,

   c) the spin cables are pulled out of the cans via an intake device and a comb and are supplied to a drawing bench, in which they are stretched at 20 to 100 °C in at least one stretching step, possibly thermofixed and relaxed at a maximum temperature of 210 °C, where the production speed is 25 to 400 m/min, whereupon they are cooled to below the glass transition temperature and, after being combined into at least one cable, are creped in one stuffing chamber creping machine per cable, the cables are possibly post-treated with an oil-water mixture and are then dried at 30 to 200 °C within 0.5 to 10 min and finally, in an immediately following or separate operation, cut to discontinuous fibers.

4. Process according to claim 3, characterized by the fact that $T_L = T_s \pm 15$ °C in the range of 234 to 290 °C and the wall shear rate of the PTT melt in the product line is 2 to 128 sec^{-1}.

5. Process according to claim 3 or 4, characterized by the fact that the product line in step a) alternatively contains at least one static mixing element, booster pump, polymer filter, polymer heat exchanger, shut off and distributor fitting and the wall shear rate of the PTT melt in the free product line is 3.5 to 16 sec^{-1} and within a static mixing element 12 to 128 sec^{-1}.

6. Process according to one of the claims 3 to 5, characterized by the fact that the nozzle hole diameter D is selected according to

$$\sqrt{\frac{F(g/min)}{\zeta(g/cm^3)\cdot\pi\cdot 2}} \geq D(mm) \geq \sqrt{\frac{F(g/min)}{\zeta(g/cm^3)\cdot\pi\cdot 7}}$$

and $T_B(°C) = T_s + dT_w + 4/100 \quad dp(bar) \pm 15$, where ζ is the density of the PTT melt, dT_w is the change of the melt temperature in the heat exchanger, which made to be is positive for heating and negative for cooling, and dp(bar) is the overall pressure loss of the melt to its exit from the spinneret plate.

7. Process according to one of the claims 3 to 6, characterized by the fact that the air-cooling zone length is 150 to 600 mm with a radially incident air stream and 500 to 2000 mm with a transverse air stream.

8. Process according to one of the claims 3 to 7, characterized by the fact that the stretching ratio SR is set according to $SR(\%) = 1 + \alpha \quad R_d/100$, where R_d is the elongation of the spun fiber in % and $\alpha = 0.25$ to 0.75, and the exit speed from the relaxation zone is at least 90 m/min.

INTERNATIONAL SEARCH REPORT

Interna tal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D01F6/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
PAJ, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 12, 29 October 1999 (1999-10-29) & JP 11 189938 A (TORAY IND INC), 13 July 1999 (1999-07-13) abstract	1-8
A	GB 1 254 826 A (FIBER INDUSTRIES INC) 24 November 1971 (1971-11-24) the whole document	1-8
A	WO 95 22650 A (DEGUSSA ;HIRT PETER (DE); KUEHL GILBERT (DE); PIANA HERMANN (US);) 24 August 1995 (1995-08-24) the whole document	1-8

☐ Further documents are listed in the continuation of box C. ☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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